Reversible Phase Transition of 4-Ethoxybenzenammonium Iodide

Wen-Xiang Wang*^[a] and Xue-Qun Fu^[a]

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Abstract. A new phase transition compound 4-ethoxybenzenammonium iodide (1) ($C_8H_{12}ON^{+}\cdot\Gamma^{-}$) was determined. Differential scanning calorimetry (DSC) results show sharp peaks appear at 157.93 K (-115.22 °C) on heating and 157.00 K (-116.15 °C) on cooling with $\Delta H = 120.34 \text{ J}\cdot\text{mol}^{-1}$, $\Delta S = 0.762 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The dielectric measurements appear clear slope change, which matches well as observed in

Introduction

With the capability of storing and releasing large amounts of energy when melting and solidifying at certain temperature, phase change materials (PCMs) are widely used in nonvolatile memory storage, electronics, optics, and telecom shelters.^[1,2] Most PCMs used now involve state changes from solid to liquid, such as water (from ice to water) and paraffin (from solid wax to liquid wax). However, smart PCMs with reversible structural changes without state change have long been an attractive target for scientists and also a great challenge. Generally, any kind of phase transition is accompanied by an anomaly of the dielectric constant and heat anomaly during heating and cooling process.^[3] In order to search for phase transition material, we usually judge by whether anomaly of the dielectric constant and heat anomaly of the dielectric constant and heat anomaly of

In our exploration on multiferroic compounds and searching for new phase transition materials,^[5–11] we discovered that 4-ethoxybenzenammonium iodide (1) undergoes a reversible phase transition from room temperature to a low temperature at ca. 157 K. Of great importance is the fact that 1 displays a dielectric anomaly and sharp peaks in DSC. Interestingly the similar structure compounds show no such characters.^[12] Herein, we report the synthesis, crystal structure, and dielectric properties of 1.

- E-Mail: wxwang@seu.edu.cn
- [a] Ordered Matter Science Research Center College of Chemistry and Chemical Engineering Southeast University Nanjing 211189, P. R. China
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group changes from $P2_1$ at 103(2) K to $P2_1/c$ at 298(2) K during the phase transition process. The essential difference between the two temperature structures is the relative orientation of the oxyethyl group to the benzene ring, slight displacements of the anionic iodine and the packing of the molecular species.

the DSC results. The crystal structure analyze shows that the space

Results and Discussion

Evaporation of the ethanol solution containing 4-ethoxybenzenamine and HI (45%, w/w) leads to the colorless crystals of **1** (Scheme 1)



Scheme 1. Structure of compound 1.

One of the best ways to detect whether phase transition of the compound is triggered by temperature is to perform DSC measurement to confirm the existence of heat anomaly occurred during heating and cooling process. Upon heating and cooling, the crystalline sample of compound **1** undergoes a single reversible phase transition at ca. $T_c = 157$ K, showing an endothermic peak at 157.9 K on heating and an exothermic peak at 157.0 K on cooling (Figure 1). From the DSC measurement, the value of $\Delta H = 120.34$ J·mol⁻¹ and an entropy increase, $\Delta S = \Delta H/T = 0.762$ J·mol⁻¹·K⁻¹, are obtained.



Figure 1. DSC diagram of 1.

^{*} Dr. W.-X. Wang Fax: +86-25-52090626

SHORT COMMUNICATION

The temperature-dependent dielectric response, especially in relatively high frequency range, is very useful in searching for phase transition materials in this system. The temperature-dependent changes of the real part ε' of the dielectric constant $\varepsilon^*(\varepsilon^* = \varepsilon' - i\varepsilon'')$ of the powder sample of compound 1 is presented on three selected frequencies, 10 Hz, 100 Hz, and 1 MHz. (see Figure 2) A clear slope of ε' can be seen as the structural phase transition occur in the vicinity of ca. 160 K, which matches well as observed in the DSC results.



Figure 2. Temperature dependencies of the real part of the permittivity of 1 at 10–1000 kHz.

Structural determinations, especially variable-temperature single-crystal X-ray diffraction, act as direct methods to show these structural symmetry changes to reveal microscopic mechanisms of phase transition. However, structural analysis of phase transition of a crystal compound is often difficult because small displacements of the ions are highly correlated with each other and with thermal parameters, which can result in inaccurate refined values and multiple solutions. Single crystal X-ray analysis (Table 1) reveals that the structures of the two isomorphs both contain the same basic structural unit that consists of 4-ethoxybenzenammonium cations and iodine anions. The structures of the low temperature phases (LTP) and room temperature phase (RTP) are very similar, differing only in the orientation of the oxyethyl group relative to the benzene ring, slight displacements of the anionic iodine and the packing of the molecular species. Crystal data of the title compound of RTP was refined to a wR_2 of 0.24 and LTP was correspondingly 0.27, which seems to be not as good as expected, but they clearly show how the phase transition occurs. The absolute configuration of LTP structure is determined using anomalous scattering.

A precise analysis of the important packing and interaction differences between the two structures is needed to discover how the phase transition occurs. The most obvious difference in conformation between the two phases is the orientation of the oxyethyl group relative to the benzene ring. This can be seen by comparison to Figure 3(a) and (b), where both views



Figure 3. View of the asymmetry unit of 1 with atomic numbering scheme (a) at 298(2) K and (b) 103(2) K.

Table 1. Summary	of	crystallographic	data for	compound	1	at	298	Κ	and	103 I	К.
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	1, 298 K, RTP	1, 103 K, LTP
Empirical formula	C ₈ H ₁₂ NO,I	C ₈ H ₁₂ NO,I
M _r	265.09	265.09
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1$
Temperature /K	298	103
a /Å	12.165(2),	12.079(2),
b /Å	6.9284(14),	6.9033(14),
c /Å	12.700(3)	6.1103(12)
βΙ°	97.96(3)	99.59(3)
$V/Å^3$	1060.1(4)	502.39(17)
Z	4	2
Radiation type	$Mo-K_a$	Mo- K_{α}
Absorption correction	Multi-scan	Multi-scan
Crystal size /mm	$0.45 \times 0.40 \times 0.40$	$0.45 \times 0.40 \times 0.40$
F(000)	512	256
$T_{\rm min}$ / $T_{\rm max}$	0.273 / 0.304	0.266 / 0.285
Flack parameter		0.1 (3)
h, k, l (min, max)	(-15, 15); (-8, 8); (-16, 16)	(-15, 13); (-8, 8); (-7,7)
wR_2	0.2466	0.2706
R_1	0.0874	0.1085

along the direction of benzene ring perpendicular to the paper. In the RTP structure, all non-hydrogen atoms in the 4-ethoxybenzenammonium are nearly coplanar and a mirror plan passes through the 4-ethoxybenzenammonium plan with the dihedral angle between oxyethyl group and benzene ring 7.5° , whereas in the LTP structure, the oxyethyl group deviates from the benzene ring gives the dihedral angle 99.6°, which leads to the loss of the mirror plan.

This conformation is stabilized by electrostatic interactions between cations and anions. The N1···I1, and C6···I1 distances are 3.526 Å and 4.558 Å, respectively, in the RTP structure. In the LTP structure, the corresponding values are 3.489 Å and 4.185 Å. Furthermore, the bond length of N1···C6 in the cation is decreased from1.454 Å in the RTP structure to 1.488 Å in the LTP structure. (Table S1, Supporting Information)

Beside the electrostatic interactions of the iodine ion and ammonium cation, the N–H···I hydrogen bonds are main molecule interaction. Both structures of **1** (4-ethoxybenzenammonium cations related by the translation along the *b* axis) are linked by N–H···I hydrogen bonds to form one-dimensional chains. Compared with the RTP structure, the hydrogen bond lengths [N···I 3.58 Å, N–H···I 139.6° at 298 K] decrease a little [N···I, 3.51 Å, N–H···I 136.6°at 103 K]. (Table S2, Supporting Information)

The two adjacent benzene rings are approximately vertical along c axis with the dihedral angle 86.5° in the RTP structure, whereas the corresponding rings in the LTP structure are completely parallel. From the cell packing view along the c axis, molecules in the RTP structure at 298(2) K are a little twisty and the oxyethyl units have two different orientations. In the LTP structure at 103(2) K, molecules are overlapped along c axis and the oxyethyl units have the same orientation (Figure 4).

The RTP structure shows that 1 crystallizes in a centrosymmetric space group $(P2_1/c)$ belonging to a nonpolar point group (C_{2h}) , whereas the LTP structure reveals that the mirror plane disappears, resulting in a decrease in the number of symmetric elements from four (*E*, *I*, *C*₂, and $\delta_{\rm h}$) to two (*E* and *C*₂) (space group $P2_1$). The new point group (C_2), which is a subgroup of the paraelectric phase (point group C_{2h}), obeys the Landau theory and suggests that this phase transition may be successive. At the same time, this phase transition obeying the Aizu rule, written as 2/mF2,^[13] is a continuous second-order phase transformation. A similar case occurred in triglycine sulfate (TGS), where the mirror disappears from a paraelectric phase (space group $P2_1/m$, point group C_{2h}) above TC (49 °C) to a ferroelectric phase (space group $P2_1$, point group C_2) upon a temperature decrease, halving the number of symmetric elements from four (E, I, C_2 , and δ_h) to two (E and C_2) in accord with Landau second-order phase transition theory and an Aizu presentation of 2/mF2.[13,14]

Conclusions

The title compound **1** undergoes a phase transition from a paraelectric phase $(P2_1/c)$ at room temperature to a ferroelectric phase $(P2_1)$ at low temperature and meets the necessary



Figure 4. Packing diagrams (a) at 298(2) K and (b) 103(2) K of **1** viewed along the *c* axis, the dashed lines show the hydrogen bonding.

and sufficient requirements for ferroelectrics. This phase transition obeys the Landau second-order phase transition theory and an Aizu rule presentation of 2/mF2. The combined DSC measurement, dielectric measurement, and structural analysis reveal that the phase transition shows reversible characters at about 157 K.

Experimental Section

General: Chemicals and solvents in this work were commercially obtained as chemically pure and used without any further purification. Infrared spectra were taken with a Bruker Vector 22 spectrophotometer as KBr pellets in the 4000–400 cm⁻¹ region. Powder X-ray diffraction measurements were made with a Rigaku/ D-MAX diffraction system, equipped with a copper X-ray tube [λ (Cu- K_a) = 1.5406] and a graphite monochromator. The powder patterns reported are the result of addition of three single scan patterns from $2\theta = 5^{\circ}$ to $2\theta = 50^{\circ}$ at 5° per min with an increment of 0.02°. Single-crystal data were collected at 298(2) K and 103(2) K with a Rigaku SCXmini CCD diffractometer equipped with graphite-monochromated Mo- K_a radiation. DSC measurements were performed with a PerkinElmer Diamond DSC in a nitrogen atmosphere in aluminum crucibles with a heating or cooling rate of 10 K·min⁻¹. Dielectric permittivities were measured with an Agilent or a TH2828A impedance analyzer.

Preparation: Complex 1 was readily obtained as colorless lamellate crystals by slow evaporation at room temperature out of an ethanol solution of an equimolar ratio of 4-ethoxybenzenamine and hydroiodic acid. ¹H NMR (300 MHz, D₂O): δ = 7.15 (d, *J* = 9.0 Hz, 2H in phenyl ring), 6.90 (d, *J* = 9.0 Hz, 2H in phenyl ring), 3.94 (q, 2H in ethyl),

SHORT COMMUNICATION

1.19 (t, 3H in ethyl) (Figure S1; Supporting Information). **IR** (KBr): $\tilde{v} = 3414$ (s), 3126 (s), 2902 (s), 2852 (m), 1620 (w), 1575 (w), 1500 (w), 1087 (w), 962 (w) cm⁻¹ (Figure S2). The powder XRD pattern of **1** match very well with the pattern simulated from the single-crystal structure at room temperature. (Figure S3)

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-783606 and CCDC-783607 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Details of ¹H NMR, the IR spectra, as well as the powder XRD pattern of **1** (Figures S1–S3); bond lengths and angles of **1** (Table S2); hydrogen bond lengths (Table S2).

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